

## CHAPTER V

### CONCLUSION

The proposed method for the determination some first row transition metals by using thin-layer chromatography were developed. The ordinary precoated silica gel 60 plate and mixed solvent of hexane, chloroform and ethanol were chosen as stationary phase and mobile phase respectively. Separation of the metal ions was the expected difference in adsorptive mechanism of their  $\alpha$ -dioximes complex on silica gel surface. The procedures of the methods were decreased by combining *in situ* complexing formation, separation and spot visualization in one step, and the analytes on the developed plates were quantitatively determined by using a densitometer. The  $\alpha$ -dioximes, namely dimethylglyoxime (DMG), benzildioxime (DPG), furildioxime and nioxime were chosen as the complexing agents. These reagents were added into the mobile phase to formed colored complexes and enhanced selectivity and efficiency of the separation in order to improve the sensitivity and selectivity of the detection.

The optimal chromatographic conditions for separation and quantitative determination of these metal ions were studied and found that Ni(II) and Pd(II) could be separated from Cr(III), Mn(II), Fe(III), Co(II) and Cu(II) by using 0.05%w/v DMG in mixed mobile phase of  $\text{CHCl}_3$ :EtOH (9:1), 0.0075%w/v DPG in mixed mobile phase of  $\text{C}_6\text{H}_{14}$ : $\text{CHCl}_3$ :EtOH (5.7:2.8:1.5), 0.015%w/v nioxime in mixed mobile phase of  $\text{C}_6\text{H}_{14}$ : $\text{CHCl}_3$ :EtOH (1.0:7.5:1.5) and 0.075%w/v furildioxime in mixed mobile phase of  $\text{C}_6\text{H}_{14}$ : $\text{CHCl}_3$ :EtOH (1.2:7.3:1.5). The selectivity of the complex formation was also improved by using the less dipolar solvent mixture as mobile phase. The clear presence of the complexes of Co(II), Ni(II), Cu(II) and Pd(II) on the obtained chromatograms indicated that their complex formation constants were high enough to overcome the very weak ionization of the ligands. The separation of metal complexes were not influenced by the complex formation constants but it was strongly influenced by the structure of metal complexes. These conditions were satisfactory for qualitative

identification of Pd(II) and Ni(II) including further instrumental in situ quantitative determination. Fortunately spots obtained moved far enough from ligand background and good separation of Ni(II) and Pd(II) was also achieved. The reproducible  $R_f$  values of their dioximes complexes were in the optimal range 0.63-0.75. The acceptable amount of Ni(II) and Pd(II) that gave good round and compact spots were not higher than 100 ng. The developing times were quite short about 15-20 minutes.

The analytes on the developed plates were determined by using the Camag densitometer. The optimum absorbed wavelength, linearity of calibration curves, repeatability, resolution and detection limit of each metal complexes systems were investigated. All of the metal complexes strongly absorbed UV light at 270 nm except Pd-furildioxime 280 nm. The metal complexes on the developed plates were determined at the wavelengths and linear calibration lines of the metal ions were reported in the ranges of 10-40 ng for the Ni-DMG system, 100-170 ng for the Pd-DMG system, 10-80 ng for the Ni-DPG system, 20-80 ng for the Pd-DPG system, 10-70 ng for the Pd-furildioxime system, 5-25 ng for the Ni-nioxime system and 50-120 ng for the Pd-nioxime system.

The main error sources of proposed methods were sample application process and positioning the spot in the center of the measuring beam. From the data obtained, the error from sample application process is higher than the others because of manual standard and sample application. To minimize its detrimental effects on the accuracy, precision and reproducibility of the methods, special skill of the analyst are required. However, total error of whole method is below 5%RSD if the standards and samples were developed on the same plate.

The limit of detection of the metal determined by this proposed methods were 3 ng for the Ni-DMG system, 11 ng for the Pd-DMG system, 6 ng for the Ni-DPG system, 6 ng for the Pd-DPG system, 3 ng for the Pd-furildioxime system, 2 ng for Ni-nioxime system and 5 ng for the Pd-nioxime system. These values limited by the manual location and positioning of the spots.

Quantitative assay of the other metal interferences was accomplished by spotting the binary metal mixtures between the analyte and the suspected metal in various mass ratios. The results in the determination of small amount of Ni(II) by

DMG, DPG and nioxime showed that the presence of Pd(II), Cu(II), Co(II) and Zn(II) interfered seriously while Mn(II), Fe(III) and Cr(III) interfered moderately. The problems also associated in the determination of Pd(II) but more seriously. Some reluctance to the use of the proposed methods of Ni and Pd determination was due to fear of disturbing the spot intensity by this interfering metals. Triethanolamine was tested for its ability to mask those interferers by employing it in the developing solution together with the  $\alpha$ -dioxime. It was found that triethanolamine was capable in masking Mn(II), Zn(II) and Fe(III) from Ni(II) but not successful in other cases. Even if the interfering ions could be eliminated by the treatment but Ni(II) itself was similarly affected when the amount of the masking ligand applied to the developing solution was higher than 1.5 M. Clearly, spot size of the Ni- $\alpha$ -dioxime complexes were extended and their measured intensity was lessened due to much slower moving of the viscous mobile phase so the quantity of the reagent should be required relatively to the interferes. In practice, dilution of sample was prior suggested and the addition of triethanolamine was provided where necessary.

The two modified quantitative TLC procedures by means of DMG and nioxime in the developing solution were chosen to demonstrate their practical utility and reliability in a determination of Ni. The TLC with the designed developing systems provided satisfactory separation, high sensitivity and precision in determination of Ni in some certified reference alloys representing  $< 5\%$ RSD and  $< 1.0\%$  relative error. This work has been directed toward several objectives, including the refinement and simplification of the overall procedure and the use of small volumes of sample. The use of an ordinary precoated silica gel plate (2 mm thickness, 10x10 cm) and about 10 mL of solvent economized the analysis cost. The addition of the complexing agents in the mobile phase was found to be a useful way to minimize the work required and made the operation more simple and rapid and obtained TLC plate was readily or preserved for further quantitative determination by *in situ* densitometry.